

Advantages of Absolute Calibration in Small-Angle X-ray and Neutron Scattering Studies of Polymers and Colloids

George D. Wignall

Solid State Division Oak Ridge National Laboratory, Oak Ridge, Tennessee 37931-6393.

The angular distribution of the intensity of scattered radiation (X-rays, neutrons etc.) reflects the structure of the material and is measured as a function of the momentum transfer, $Q = 4\pi\lambda^{-1}\sin\theta$, where λ is the wavelength and 2θ is the angle of scatter. Because of the inverse (Fourier) relationship between the structure in real-space (D) and the scattering in Q -space ($D \sim 2\pi/Q$), data at lower Q -values probe longer length scales and these measurements are conventionally referred to as small-angle X-ray or neutron scattering (SAXS and SANS), though it is the Q -range which determines the length scale probed (typically ~ 10 - 1000\AA). This paper emphasizes the importance of placing such data on an absolute scale, in the form of a differential cross-section $d\Sigma/d\Omega(Q)$, per unit sample volume (in units of cm^{-1}). The use of absolute units is not essential for the measurement of spatial dimensions, though it forms a valuable diagnostic tool for the detection of artifacts, to which scattering techniques are particularly vulnerable. Because the cross section varies as the sixth power of the dimensions [1], it is a very sensitive indicator of whether an appropriate structural model has been chosen. Absolute calibration allows artifacts to be recognized, and the model parameters may be restricted to those which reproduce the observed cross-section, as illustrated in the following examples.

Example 1: SANS and SAXS from melt crystallized polyethylene

Figure 1a shows a Zimm plot $[(d\Sigma/d\Omega)^{-1} \text{ vs. } Q^2]$ of the SANS data from 6.0wt.% of deuterated polyethylene (PED) in a matrix of unlabeled PEH after rapidly quenching from the melt. The signal arises from the difference in scattering length between H^1 and D^2 nuclei, so that deuterated and protonated molecules have strong neutron scattering contrast. The extrapolated cross-section $[d\Sigma/d\Omega(0) \approx 28.0 \text{ cm}^{-1}]$ is proportional to the molecular weight (MW) and when the sample is rapidly quenched (crystallized) from the melt, the SANS data lead to $\text{MW} \approx 45,000$, which is of the same order as the value from chromatography [4]. However, when the

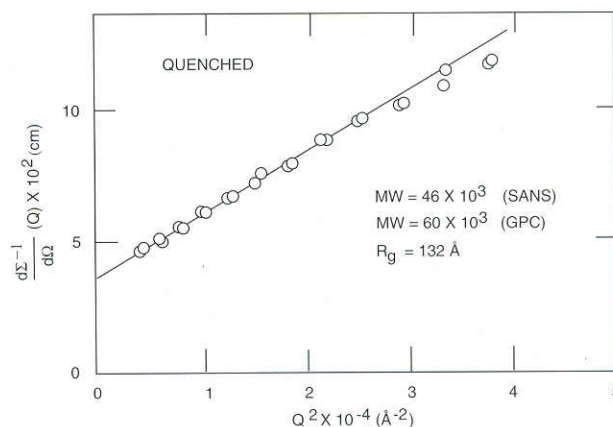


Figure 1a: Typical Zimm plot for 6% PED molecules in PEH matrix quenched from the melt.

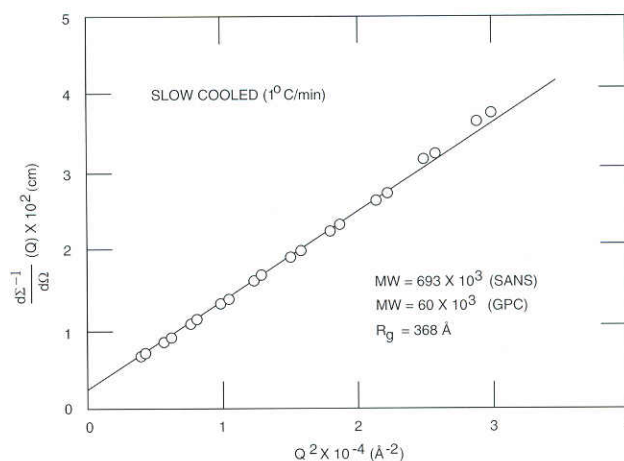


Figure 1b: Typical Zimm plot for 6% PED molecules in PEH matrix slow cooled ($1^\circ\text{C}/\text{min}$) from the melt.

same sample is slowly cooled (crystallized) from the melt, figure 1b, the apparent MW increases by over an order of magnitude. It is clear that these data do not originate in the scattering from single molecules, and it has been shown that the excess intensity is caused by aggregation or clustering of the D-labelled molecules [2], due to the difference in melting point ($\sim 5^\circ\text{C}$) between protonated and deuterated species. On slow cooling, the PEH crystallizes first, leading to a non-uniform distribution of PED in PEH as illustrated schematically in figure 2, though rapid quenching does not allow time for such a separation to develop. This artifact would not be apparent if the data were in arbitrary units, thus illustrating the point referred to above, that the intensity is extremely sensitive to the dimensions and even an approximate ($\pm 25\%$) absolute calibration is sufficient to reveal the presence of such inhomogeneities.

In the case of a sample of pure deuterated polyethylene (PED), the signal arises from the density difference between the alternating crystalline and amorphous regions in the lamellar stack, and it

Measure MW VIA CHROMATOGRAPHY (MW-GPC)
AND ALSO VIA SANS (MW-SANS)
MW-SANS ~ MW-GPC (RAPIDLY QUENCHED FROM MELT)
MW-SANS >> MW-GPC (SLOWLY COOLED FROM MELT)

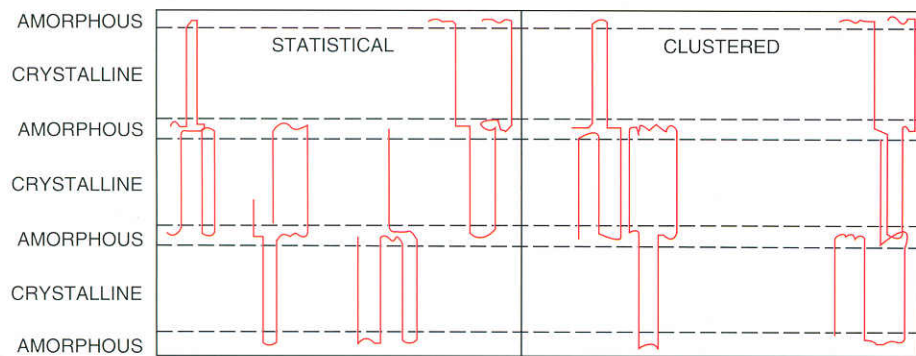


Figure 2: Aggregation or clustering of deuterium-labelled (PED) in protonated (PEH) polyethylene matrix. The D-labelled molecules form aggregates on slow cooling due to the melting point difference ($\sim 5^\circ\text{C}$) between PEH and PED.

may be shown [5] that the SAXS and SANS cross-sections are virtually identical, apart from a scale factor. Figure 3 shows absolute SAXS and SANS data for the same sample of PED and the theoretical ratio of the two signals (1.27) is in good agreement with the measured ratio (1.31 ± 0.1), thus giving a cross check on the validity of the independently calibrated SAXS and SANS data.

Example 2: Blockcopolymer Micelles in Supercritical Carbon Dioxide

Supercritical CO_2 presents an environmentally benign medium for polymerizations which minimizes the production of organic solvent and aqueous wastes. However, only two classes of polymeric materials (amorphous fluoropolymers and silicones) have been shown to exhibit appreciable solubility, and this necessitates the use of stabilizing moieties (surfactants) to emulsify CO_2 -insoluble polymers such as polystyrene. SANS and SAXS methods allow the elucidation of the size and shape of both individual molecules and also supramolecular structures [6,7] and this lecture

presented some of the first data that have been taken to characterize micellar structures in CO_2 . For example, styrene has been polymerized in CO_2 by means of a polystyrene-*b*-polyfluoro-octylacrylate (PS-*b*-PFOA) block copolymer surfactant, which solubilizes the polymer in CO_2 in much the same way as detergents may be used to solubilize oil in water via the formation of microemulsions, as illustrated schematically in figure 4. The experiments to characterize these colloidal aggregates were performed on the ORNL SAXS and SANS facilities [8,9] and the intensities were converted to an absolute ($\pm 4\%$) differential cross-section per unit sample volume [$d\Sigma/d\Omega(Q)$] by comparison with pre-calibrated secondary standards [5,10].

The first small angle scattering study of aggregation mechanisms of copolymer micelles in supercritical CO_2 was undertaken [11] on H_2O -swollen PFOA-*g*-polyethylene oxide graft copolymers using

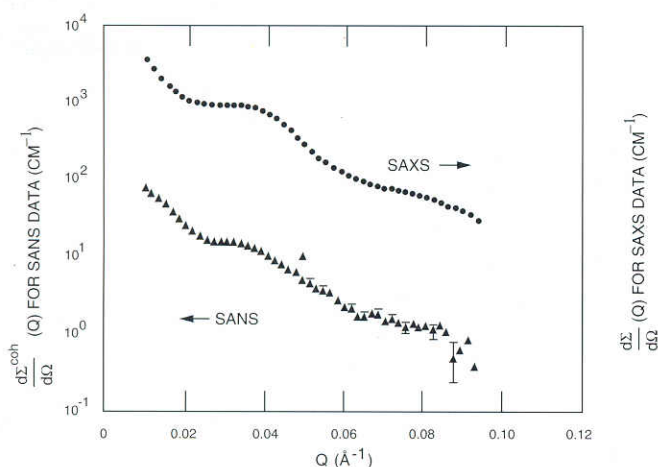


Figure 3: $d\Sigma/d\Omega(Q)$ vs Q for deuterated polyethylene sample after subtraction of incoherent background

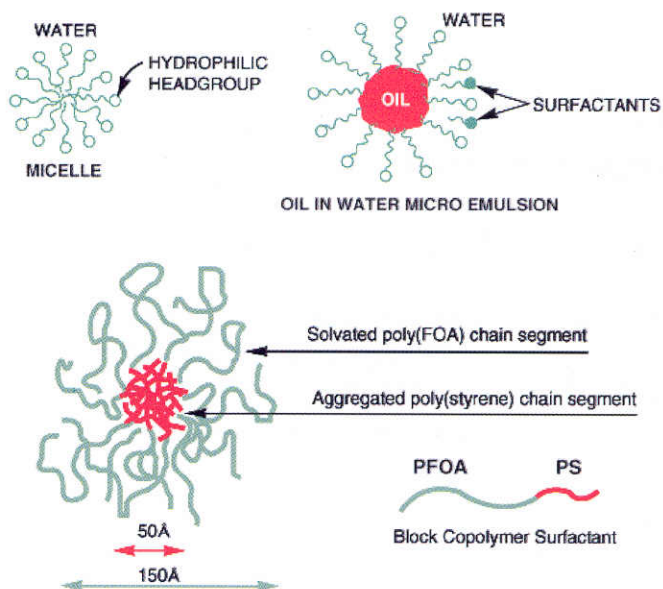


Figure 4: Schematic representation of colloid aggregates in water and supercritical carbon dioxide (above) and model of poly(FOA-*b*-styrene) micelle in supercritical CO_2 (below).

contrast factors, and hence the weighting of the components of the structure are quite different for the two techniques.

In order to minimize the time associated with calibration procedures, emphasis is placed on developing pre-calibrated, strongly scattering standards [5,9] which may be run in brief time periods (~1 minute), and figure 6 shows a polyethylene SAXS standard, which has been calibrated with respect to the ORNL suite of SAXS standards [5] for the Daresbury synchrotron SAXS facilities. The peak at $Q \sim 0.0227 \text{ \AA}^{-1}$ is due to the periodic stacking of crystalline lamellae alternating with amorphous regions, with a period $\sim 277 \text{ \AA}$.

References

- [1] A. Guinier and G. Fournet, *Small-Angle Scattering of X-Rays*, Wiley, New York, (1955).
- [2] J. Schelten *et al.*, *Polymer*, **18**, 1111, (1977).
- [3] J. B. Hayter and J. Penfold, *Colloid and Polym. Sci.*, **261** (1983) 1022.
- [4] J. Schelten, D.G.H. Ballard, G. D. Wignall, G. Longman, and W. Schmatz, *Polymer*, **27**, 751, (1976).
- [5] T. P. Russell, J. S. Lin, S. Spooner and G. D. Wignall, *J. Appl. Cryst.*, **21**, 629 (1988).
- [6] D. Chillura-Martino *et al.*, *J. Molecular Structure*, in press.
- [7] J. D. Londono *et al.*, submitted to *J. Appl. Cryst.*
- [8] W. C. Koehler, *Physica* (Utrecht), **137B** (1986) 320.
- [9] G.D. Wignall, J.S. Lin, and S. Spooner, *J. Appl. Cryst.*, **23**, 241, (1990).
- [10] G. D. Wignall and F. S. Bates, *J. Appl. Cryst.*, **20** (1986) 28.

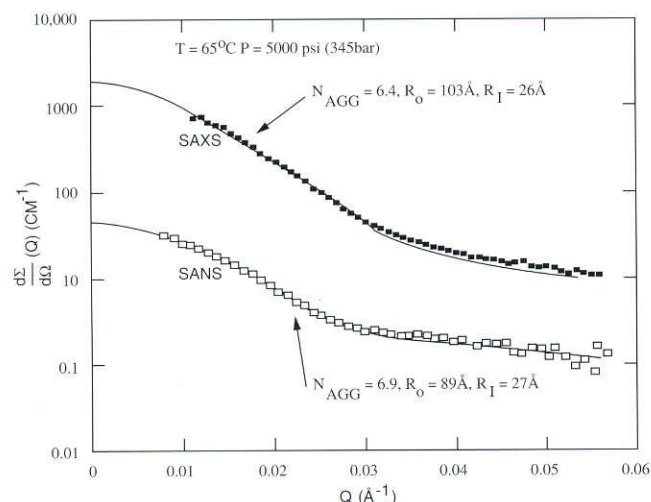


Figure 5: $d\Sigma/d\Omega(Q)$ vs. Q for independently calibrated SAXS (solid squares) and SANS (squares) data from 4k/40k PS-PFOA block copolymer micelles in CO_2 .

SAXS, though no calibration of the data was attempted. When this was subsequently accomplished, the initial model parameters were not able to reproduce the measured cross section. Neutron and X-ray scattering are complementary techniques that highlight different components of the structure and we have constructed a high-pressure SAXS cell based on the original design of Fulton and co-workers [11] to facilitate such comparisons. Figure 5 shows a comparison of SAXS and SANS data taken from 4k/40k PS-b-PFOA block copolymer solutions at similar experimental conditions, which were fitted to a spherical core-shell model [7]. The neutron and X-ray cross sections were calibrated independently using secondary standards as explained above. The values of the core radius (R_I) and the aggregation number (i.e. the number of molecules per micelle, N_{agg}) were virtually identical for SAXS and SANS. This forms a useful cross check on the validity of the methodology, as the

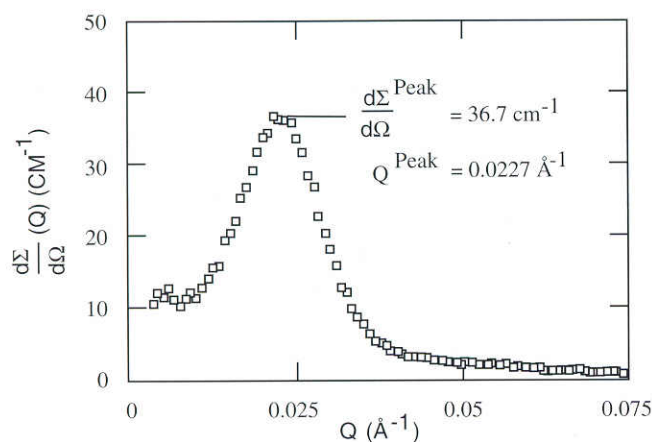


Figure 6: $d\Sigma/d\Omega(Q)$ for S-2907 pre-calibrated SAXS standard

